Influence of counter ion on polyaniline and polypyrrole

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Abstract. The electronic, magnetic, optical and redox properties of conjugated polymers are greatly influenced by structure, electronegativity, solvation and orientation of a counter ion. The doping by counter ion not only creates a band structure but also stabilizes localized bound states to impart unusual optical and magnetic properties to macromolecular system. When the polymer is in contact with solution of an electrolyte, counter ion tends to be solvated and mobile in the polymer phase, imparting it a property of ion exchange membrane. Here we briefly summarize the influence of anion on properties and electrochemical behaviour of polyaniline and polypyrrole.

Keywords. Anion; polyaniline; processibility; intractable; protonation.

1. Introduction

The past two decades have witnessed unabated interest in the synthesis and characterization of conjugated polymers that display unusual solid state properties (Trivedi and Srinivasan 1988; Trivedi 1989). The polymers most widely studied up till now are: (i) having a generalized structure, $[-A-]_n$, where A is an aromatic ring like pyrrole, benzene or thiophene, or (ii) having a generalized structure $[-AB-]_n$ where A is phenyl and B is $-NH-$ imine in polyaniline. These polymers as synthesized are macromolecular cations and hence for the reason of charge compensation they take up counter ion from the electrolyte. Thus the electronic, magnetic and optical properties of polymers become the function of dopant. Due to metallic conductivity these systems are intractable and hence their processibility is a challenge. The conductivity and processibility are twin phenomena, requires the use of concepts which bridge electrochemistry and organic chemistry on the one hand, with the field of condensed matter science on the other. Particularly interesting are systems whose composition can be selectively altered, thereby leading to varying electronic properties for the development of new material having a processibility of a plastic, and electronic conductivity of a metal or a semiconductor.

During the detailed studies on use of variety of dopants, we observed that conductivity and processibility of polyanilines not only depends on protonation level but also is strongly influenced by counter anion. Similarly it has been found that pyrrole on polymerization yields a powdery material in aqueous sulphuric acid medium (Dall'Olio *et al* 1968), whereas in presence of BF_4^- , ClO_4^- and PF_6^- under nonaqueous condition gives a free standing film (Diaz *et al* 1979). Recently it has been shown that introducing large size dopants (Zhong *et al* 1990), can

alter ion exchange property of a polypyrrole (PPy) film. Thus electrical conductivity, thermal stability, processibility, and electrochemical growth not only depends on oxidation state of a polymer but are also dependent on the nature of counter anion which can be defined in terms of its electronegativity, molecular size, orientation and solvation (Trivedi 1997; Zotti *et al* 1988).

Polyaniline has been known almost for 136 years as aniline black (Letheby 1862). However, its systematic synthesis and structure are of recent origin (MacDiarmid *et al* 1985). Polyaniline (PA) though environmentally stable is intractable. Polyaniline is built from reduced ($-B-NH-B-NH-$) and oxidized ($-B-N=Q=N-$) repeating units, where B denotes a benzenoid and Q denotes a quinoid ring. Thus the different ratios of amine to imine yield various structures, such as leucoemeraldine (a reduced form), emeraldine base (neutral undoped form), emeraldine salt (50% oxidized, doped form), and perinigraniline (fully oxidized form). The various forms are shown in figure 1. The conductivity of polyaniline depends not only on oxidation state but also on the degree of anions, to maintain charge neutrality. This suggests that the behaviour of polyaniline depends on the pH as well as on the counter ion of the Bronsted acid used for doping. The protonation equilibria involves exclusively the quinone diimine segment of the polymer chain, having two imine nitrogens with $pK_{a1}=1.05$ and $pK_{a2}=2.5$ (Haug *et al* 1987). The protons are added to $-N=$ sites while the number of electrons in the chain remain constant (Schacklette *et al* 1988). However, the functionality present in the dopant determines its processibility. Cao *et al* (1992) reported that when camphor 10 sulphonic acid is used as dopant, the resulting polymer is soluble in solvents like chloroform. Therefore, it is reasonable to expect that electrochemical and other properties of the conductive polymer will

be influenced by the nature of the incorporated counter ion.

Polypyrrole (PPy) is known since 1916 (Angeli 1916), however, its semiconducting properties were first investigated by McNeill *et al* (1963). PPy was first electrochemically synthesized as a black powdery deposit in aqueous sulphuric acid medium anodically by Dall'Olio *et al* (1968). In 1979 (Diaz *et al* 1979) reported electrochemical synthesis of an electrically conducting free standing film of good mechanical strength. The electrochemical method facilitated incorporation of variety of counterman into polymer film. Since the oxidation potential of PPy is lower than that of monomer, thus the polymer is simultaneously oxidized during polymerization and hence counter ions from electrolyte are incorporated into growing polymer in order to maintain electrical neutrality.

Polypyrrole (PPy) can be viewed as a carbon chain with structure of polyacetylene stabilized by the heteroatom and has a nondegenerate ground state related to nonenergetic equivalence of two limiting mesomeric

forms, aromatic and quinoid. In polymerization of pyrrole, the first step consists of the oxidation of the monomer to its radical cation. The second step involves the coupling of two radical cations to yield a dihydrodimer dication that leads to a dimer after loosing two protons and rearomatization. The dimer has less oxidation potential than monomer, undergoes further coupling with a monomeric radical, subsequently electrochemical and chemical steps occur until oligomer becomes insoluble in the electrolyte and precipitates on to the electrode surface. In pyrrole polymerization presence of water is essential to eliminate protonation of pyrrole and therefore, the conductivity of PPy decreases as the anion basicity increases. The polymerization process requires 2.2–2.4 Faraday/mole. 2 Faraday are required for the oxidation of monomer and the remaining are required to generate the macro cation. Thus this corresponds to reversible oxidation (doping) of the polymer.

The doping–dedoping is a complex phenomena governed by many factors, such as ion pair formation which can occur within the doped polymer between the dopant and positive charge on the polymer chain, resulting in the diffusion of cation from electrolyte to keep polymer chain electrically neutral. These cationic species owing to their smaller ionic size have greater mobility, therefore continuous doping–dedoping by cycling the polymer electrode between extreme potential limits yields a polymer free from ion pair as well as from oligomeric impurities. Therefore, it is inevitable that kinetics of doping–dedoping and polymerization is influenced by steric effects associated with counter ion like:

- adsorption on working electrode;
- redox potential;
- the ionic charge;
- ionic size;
- solvation shell;
- ionization constant of the electrolyte;
- concentration of electrolyte;
- electrochemical potential of doping;
- diffusion coefficient of a dopant, which varies with solvent, concentration of electrolyte, temperature and applied potential.

These aspects are important because polymer undergoes substantial volume changes during doping and dedoping processes. These dimensional changes influence mechanical strength of a polymer and have been utilized to convert electrical energy to mechanical energy (Baughman 1996).

Not all dopants can induce charge transport in polymer. The charge transport depends upon the redox energy of the host and guest molecules because transfer of an electron is from high to low redox energy. Initially the charge transfer on doping is between the dopant molecule and the proximal polymer site, but subsequently some diffusion of polymer charge to the dopant site can be

Figure 1. Various forms of polyaniline: (a) leucoemeraldine; (b) emeraldine base; (c) emeraldine salt; (d) pernigraniline.

expected, generating thereby pair states in polymer. In equilibrium, the number of polymer pair states are equal to the number of ionized dopants. ESR (Javadi *et al* 1988), electron energy loss spectroscopy (Litzemann *et al* 1989), NMR (Raghunathan *et al* 1996) and thermopower studies (Raghunathan *et al* 1993) support these findings. These observations have given rise to speculation that ferromagnetism can be induced in these conjugated systems.

2. Experimental

The method of synthesis of emeraldine salt by chemical oxidative polymerization and electrochemical polymerization has been discussed in detail elsewhere (Trivedi 1997). In the present study, we used the following protonic acids as dopants for polyaniline: 2,5 dimethylbenzene sulphonic acid, 1,2-dimethylbenzene sulphonic acid, 3-chloro-4-hydroxy benzenesulphonic acid, 2-methyl-4-hydroxy benzenesulphonic acid, 4-hydroxy-*m*-benzene disulphonic acid, 2,4-dihydroxy-*m*-benzenedisulphonic acid, 2,4-hydroxybenzene sulphonic acid and oxalic acid.

The electrochemical polymerization and characterization of polypyrrole were carried out in sodium salt of dodecyl benzenesulphonic acid, lithium perchlorate and tetralkylammonium salts. Aromatic sulphonic acid used in these studies was synthesized and purified as per standard synthetic organic chemistry methodologies.

X-ray diffractograms for all polymers were recorded using CuK_α radiation ($\alpha = 1.5418 \text{ \AA}$). The diffused reflectance UV-visible spectra for thin films were recorded on Hitachi-U-3400 spectrophotometer and FTIR in KBr medium on Perkin Elmer FTIR spectrometer. Thermal studies were carried out under nitrogen at flow rate of 100 ml/min with heating rate of 20 C/min on Perkin Elmer 7 thermal analyser.

The cyclic voltammetric studies were carried out using Tacussel BI-PAD Bipotentiostat coupled with an X-Y recorder (BBL model SE 780) and PARC universal programmer. The 0.25 cm^2 platinum electrodes were used. All electrode potential values reported in this paper are referenced to saturated calomel electrode (SCE).

All chemicals used were analytical grade. All solutions were thoroughly purged with Ar. The platinum electrodes were polished with finer grade alumina ($0.05 \mu\text{m}$) before use.

3. Results and discussion

3.1 Electrochemical studies

3.1a Polyaniline: The cyclic voltammetric studies during growth of a polymer film suggests that on passing same amount of current under identical conditions thicker

polymer film formation occurs in the presence of oxidizing ions like NO_3^- and ClO_4^- (Duic *et al* 1994). However, the anion which promotes the growth of polymer are also responsible for degradation of polymer film by resulting in over oxidation. The general mechanism for oxidative polymerization of aniline at pH1 and its simultaneous degradation are illustrated in equation (1). Thus, according to this equation two parallel sets of reaction occur: polymer growth and its degradation. As the polymer builds up, delocalization also increases which inhibits the autocatalytic growth of the polymer leading thereby to oxidative degradation of the dimer to quinone.

3.2 Cyclic voltammetric studies

The growth pattern of polyaniline in benzenesulphonic acid is given in figure 2, where a middle peak indicates the degradation to quinone during synthesis. This position of middle peak due to quinone was confirmed by adding quinone during synthesis. The growth of the polyaniline film on electrode substrate was performed by a cyclic potential sweep method by switching the potential between -0.2 and $+0.8 \text{ V}$ vs SCE for aromatic sulphonic acid and -0.2 to 1.0 V vs SCE for oxalic acid medium by passing charge of 0.32 C/cm^2 . The cyclic voltammetric (CV) response of the polyaniline film was recorded in an electrolytic medium (without the monomer); the peak potential values are given in table 1.

The cyclic voltammogram (figure 3) gave three peaks in all cases except oxalic acid. The first oxidation peak is assigned to the transfer of a single electron giving rise to a radical cation, and the third peak to the transfer of another electron leading to the formation of diradical

Equation (1). Polymerization mechanism of aniline to polyaniline.

Table 1. Electrochemical data on polyaniline.

Aromatic sulphonic acid	Anodic			Reference
	I peak	II peak	III peak	
2,5-Dimethylbenzene sulphonic acid	0.170	—	0.620	This work
1,2-Dimethylbenzene sulphonic acid	0.580	—	0.860	This work
3-Chloro-4-hydroxybenzene sulphonic acid	0.200	—	0.500	This work
2-Methyl-4-hydroxybenzene sulphonic acid	0.170	—	0.500	This work
4-Hydroxy- <i>m</i> -benzenedisulphonic acid	0.180	—	0.580	This work
2,4-Dihydroxy- <i>m</i> -benzenedisulphonic acid	0.220	—	0.670	This work
4-Hydroxybenzene sulphonic acid	0.180	—	0.540	This work
5-Sulphosalicylic acid (> 0.8 V), (< 0.8 V)	0.140	0.460	0.720	Trivedi and Dhawan (1993a, c)
<i>p</i> -Toluenesulphonic acid	0.100	0.410	0.710	Trivedi and Dhawan (1993a, b)
Benzenesulphonic acid	0.130	0.400	0.700	Dhawan and Trivedi (1993a)
Sulphamic acid	0.125	0.400	0.670	Dhawan and Trivedi (1991)
Sulphuric acid	0.090	0.360	0.625	Dhawan and Trivedi (1992)
Oxalic acid	0.240	—	0.460	—

dication, followed by loss of two protons as given in equation (2). The middle peak is assigned to the hydrolysis product of the polymer like benzoquinone or hydroquinone as shown in equation (1); which gets entrapped in

Figure 2. Growth pattern of polyaniline in 1 M benzene sulphonic acid (aniline, 0.1 M; sweep rate, 50 mV/sec).

polymer matrix during synthesis. However, such degradation is ruled out in presence of reducing anions like oxalate. It has been observed that polyaniline film grown in a reducing medium like oxalic acid has a very high stability. In this system the surface electron transfer occurs at 240 mV and protonation around 460 mV vs SCE. This narrow potential range observed in oxalic acid medium is particularly suitable for electrochromic display due to reduction in time required for cycling the film between extreme potentials. The growth of polyaniline in 1 M oxalic acid is given in figure 4 to show how the degradation of polyaniline can be minimized.

3.2a Membrane properties of polyaniline: The membrane properties of polyaniline were investigated on electro-deposited polyaniline on platinum electrode of 1 cm². We found that the slope in the curve of potential vs log(C) concentration were less than 59 mV indicating that in addition to anion transport cation transport also

Equation (2). Explains the CV peaks of polyaniline.

occurs. Slopes of 45–50 mV were observed for F^- , Cl^- , Br^- , NO_3^- , and ClO_4^- , whereas slope of 15 mV was observed in aromatic sulphonate medium indicating that anion size influences transport across the membrane.

At pH1 in aromatic sulphonic acid medium negative slopes were observed indicating that anion permeability decreases and H^+ are exchanged.

3.2b Electronic spectra: The diffused reflectance spectra on platinum substrate gave well-resolved peaks at 320–330 nm, 420–430 nm and 790–900 nm. These peak positions were found to be dependent on doping level. At 25% doping level absorption peaks were observed at 317, 410 and 670 nm and at 50% doping level (maximum achievable doping level) peaks were observed at 320, 420 and 840 nm. The (π – π^*) transition was observed at 427 nm due to semiquinone structure and band due to trapped excitons was found around 648 nm in polyaniline–oxalic acid system, however, in all other systems it was observed at 850 nm. The polyaniline film grown in oxalic acid, on dedoping and redoping in sulphuric acid medium, the 648 nm band shifts to 850 nm due to bipolarons, suggesting that absorption band at 648 nm

in PAN–oxalic acid system is not due to lower conjugation in polymer but is essentially due to polarons.

3.2c 1H NMR studies: The 1H NMR of doped (with various dopant) polyaniline in $DMSO-d_6$ gave broad resonance aromatic peaks around 7.6 and 7.18 ppm due to aromatic protons of the aniline ring system. The NH proton signals were observed between 3.8 ppm and 3.6 ppm. In all the cases undoped samples gave aromatic proton signals at 7 ppm and NH proton signal at 3.34 ppm.

3.2d FTIR studies: The main FTIR characteristic bands observed in KBr medium are:

Nitrogen-benzenoid-quinoid	– 1572–1560 cm^{-1}
N–H stretching	– 1490–1495 cm^{-1}
C–C stretching	– 1300–1303 cm^{-1}
C–N stretching	– 1250–1260 cm^{-1}
SO ₂	– 1170–1160 cm^{-1}
C–H band	– 1130–1140 cm^{-1}
SO ₃ –	– 1020–1040 cm^{-1}
C–H out of plane	– 798–802 cm^{-1}

The C–H out of plane band 798–802 cm^{-1} indicates the para coupling in the polymer.

Figure 3. Cyclic voltammogram of polyaniline in 1 M benzene sulphonic acid (Sweep rate, 50 mV/sec).

3.2e Electron spin resonance: In all cases, room temperature ESR-line exhibits pronounced asymmetry with A/B ratio at about 1.4. This ratio decreases to 1.2 at 77 K. The electrochemically synthesized PPy film gave $g = 2.0024$, and ΔH_{pp} 0.969 G. Polyaniline gave $g = 2.0028$ and ΔH_{pp} 4.95 G. In case of polypyrrole, line shape remained unchanged from room temperature to liquid nitrogen temperature indicating strong paramagnetism (detailed study would be reported elsewhere).

3.2f X-ray diffraction: In all cases broadening of peaks occurs indicating amorphous nature of materials. The four sets of 2θ values were observed ranging from 18 to 26.

3.2g Thermal stability: In all cases first weight loss (3%) occurs between 60–100°C due to moisture. However, the stability of a doped state becomes the function of a dopant. The dopant loss was found to be around 40% by weight. The data are recorded in table 2.

The anion effect is possibly related to the hydration shell of anion as suggested by Desilvestro and Scheifele (1993) who have shown that the hydration enthalpies and Gibbs free energies show a good correlation with polymerization rates. However, onset potential for oxidation (polymerization) of aniline is independent of anion and its self-catalyzing reaction and obeys the law $1/nFA = Kc$, where Kc is the autocatalytic rate constant

and has a value of approximately 0.47 s^{-1} for a film of 140 nm (Shim and Park 1989).

The use of aromatic functionalized sulphonic acid as a dopant induces certain changes in properties of poly-

Figure 4. Growth of polyaniline in 1 M oxalic acid (aniline 0.1 M; sweep rate, 50 mV/sec).

Figure 5. Various defects in the polypyrrole (PPy) structure in presence of oxidizing anions.

aniline via formation of ternary system involving polymer, dopant and solvent. Solvation of polyaniline is a result of a number of interactions between polymer dopant and solvent such as Borne-type, hydrogen bonding, hard-soft acid base interactions and Lewis acid base (donor-acceptor interactions). The change in structure of polymer cannot be ruled out due to restructuring of the solvent in presence of ions. Thus functionalized protonic acid yields a DMSO, chloroform, xylene and various common organic solvent soluble conducting polyaniline, from which free standing film can be easily obtained.

Currently, research in polyaniline is centred around finding a suitable dopant that can induce formation of blend with commercially viable polymers such as polyolefins, polyesters, poly(methyl methacrylate). In these systems, counter ion acts as a surfactant, for example dodecyl benzene sulphonic acid and camphor sulphonic acid can yield a polyblend with polymethyl methacrylate with 2% polyaniline with electrical conductivity of 100 S cm^{-1} (Heeger 1995). Studies have indicated that using suitable dopant polyaniline can find applications in control of EMI shielding (Trivedi and Dhawan 1993a, b, c), batteries (Kumar *et al* 1996), corrosion inhibitors (Sathyanarayan *et al* 1992, 1994; Dhawan and Trivedi 1993a, b 1995) and as sensors (Dhawan *et al* 1997).

3.3 Polypyrrole [PPy]

Polypyrrole is one of the polymers that has attracted equal attention from physicists and chemists, because of its simplicity of structure and low oxidation potential which favours the formation of 2,5-bonded polymer as a free-standing film on an anode surface. The polymerization of pyrrole can be effected in presence of host of electrolytes under aqueous or nonaqueous conditions. Due to low oxidative polymerization potential, pyrrole can be polymerized by vapour phase oxidation in presence of suitable mild oxidant, e.g. ferric ion (Dhawan and Trivedi 1993a, b). Due to low oxidation potential of polypyrrole than polymerization potential of pyrrole, the oxidizing anions like NO_3^- and ClO_4^- in presence of protonic impurities can yield a polymer having other than 2,5 linkage having a carbonyl and hydroxyl group (see figure 5). Thus conjugational length depends on the syntheses conditions, like temperature, concentration of monomer and electrolyte and electrochemical potential. At lower electrochemical potential conjugational defects are reduced because of slower rate of reaction. Lowering the temperature during synthesis can further lower the rate of reaction. The polymerization mechanism is given in equation (3).

A unique aspect of the electrochemical behaviour of the polypyrrole film is that it is inherently redox electroactive. The broad peak and its shape in cyclic voltammogram (figures 6 and 7) suggest that redox reaction

Table 2. Thermal stability of electrochemically synthesized polyaniline.

Dopant	Moisture expulsion temperature (°C)	Dopant expulsion temperature (°C)	Decomposition temperature (°C)
5-Sulphosalicylic acid	80	238	472
2,4-Dihydroxy- <i>m</i> -benzene disulphonic acid	71	369	472
2-Methyl-4-hydroxy benzenesulphonic acid	100	468	549
2-Hydroxy benzene sulphonic acid	60	329	638
2,5-Dimethyl benzene sulphonic acid	64	455	654
4-Hydroxy benzene 3,6 disulphonic acid	90	356	700

Table 3. Electrochemical data on polypyrrole.

Electrolyte	E_{pa} (mV)	E_{pc} (mV)	Conductivity (s/cm)
<i>In Acetonitrile</i>			
LiClO ₄	-110	-440	100
Me ₄ NPF ₆	-160	-325	50
Et ₄ NBF ₄	-100	-300	20
Et ₄ NClO ₄	-090	-290	100
Bu ₄ NBF ₄	-110	-260	20
<i>In aq. medium</i>			
Dodecylbenzene sulphonate	+170	-070	01

Figure 6. Cyclic voltammogram of polypyrrole at 50 mV/sec and 100 mV/sec in (CH₃)₄NPF₆, (C₂H₅)₄NClO₄, (C₄H₉)₄NBF₄, (C₄H₉)₄NClO₄.

of polypyrrole is not strictly Nernstian. This behaviour indicates slow ion mobility in the polymer film. Using tetraalkyl ammonium salt (fluoroborate and perchlorate), we found that 10% excess of charge gets consumed, indicating that four pyrrole units consumed one electron to give a macro cation.

It is not clear to what extent the broadening of peak is due to repulsive interactions between the electroactive sites and/or due to the electrochemical non-equivalence of the sites. In all cases peak width are more than 90 mV, which is not expected for surface electron transfer reaction.

As can be seen from cyclic voltammograms, using various tetraalkyl salts, that the electrolyte Bu_4NBF_4 influences reduction reaction, while Bu_4NClO_4 influences oxidation reaction (figure 6). When we replaced tetraalkyl salt by sodium dodecyl benzene sulphonate using aqueous medium, the peak observed were very broad, and cathodic peak at higher sweep rate tended to bifurcate indicating the retention of the large surfactant anion in the polymer matrix during reduction process (figure 7). This behaviour indicates that fixed anionic charges can be incorporated on polypyrrole film to be utilized as the ion exchange membrane.

Table 3 summarizes some of the electrochemical parameters on polypyrrole in presence of various dopants.

Cyclic voltammogram (Pt) polypyrrole (20nm thick) in 0.1M Sodium dodecyl benzene sulphonate.

Figure 7. Cyclic voltammogram of polypyrrole at 50 mV/sec and 100 mV/sec in 1 M aqueous solution of dodecyl benzene sulphonate.

3.3a Electrochemical growth: The growth of conducting polymer film has been a subject of intensive studies by various techniques to understand its various properties like ion transport and optical. In principle, the growth of the conducting polymer can be compared with electrodeposition of metals, the difference being that the former is an anodic reaction. The filming of an anode surface during electrolysis of a monomer in a suitable electrolytic medium occurs via oxidative generation of radical cations near the vicinity of an anode which on further coupling leads to precipitation of conducting polymer leading to filming of an anode surface suggesting that particles are added one at a time to a cluster or aggregate of particles via random walk trajectories that is to say that competing growth of polymer from anode surface leads to formation of a cluster. This formation of a cluster can be considered as an alloy of macro-molecule with counter ion giving it a distinct entity.

The electrodeposition reaction from solution phase is a transformation reaction, thus there is a tendency in the system between order and disorder, which results in thermodynamic fluctuations leading to formation of disordered phase. For example Kim *et al* (1991), using ellipsometry as a tool, have reported that during polypyrrole deposition from 0.2 M aq. potassium nitrate solution, at first the film grows linearly up to 15 nm in 50 s and its thickness stays constant up to 150 s, then once again thickness increases at a constant rate till it reaches 35 nm. It has been suggested that this behaviour is due to densification of polymer film, suggesting that first there is monolayer formation to thin fibrous layer which is followed by a thick granular layer. EQCM experiments on growth of PPy suggests that initially soluble oligomer formation occurs, which upon further polymerization precipitates on anode surface. The frequency response during electropolymerization suggests second-order dependency of polymerization on monomer concentration, indicating bimolecular coupling of oxidatively formed radical cation is the rate-determining step.

During polyaniline polymerization in presence of 1 M aromatic sulphonic acid of a constant ionic strength there is continuous rise in current after an initial decay, suggesting parallel nucleation along with autocatalytic growth of polyaniline. This aspect can be explained by analysing cyclic voltammogram (CV) during the growth of polymer by potentiodynamic method (figure 2). It can be seen from CV that relatively broad peak appears at potential significantly less positive than required for bulk oxidation of monomer, sharp peaks resulting from nucleation and monolayer spreading follow this. The sharp rising of these peaks suggest the formation of two dimensional patch and expanding in a shape preserving way. The close similarity of peaks in repeated cycles with increasing current suggests that nucleation occurred repeatedly on same site resulting in a nucleus on top

of the still growing monolayer. The initial decay and then increase in current suggests that polymer formation is by random nucleation, however, we were able to observe the step type of transients in both polypyrrole and polyaniline electropolymerization by potential step technique in presence of highly functionalized dopants suggesting the formation of a layered structure. Similar type of behaviour has been reported (Li and Alberty 1992) for polymerization of thiophene-3-acetic acid.

4. Conclusion

Intercalated polyaniline and polypyrrole exhibit variety of properties depending upon stoichiometries and functional groups associated with dopant owing to their electrostatic interactions and vander Waals interactions by either close contact/overlap or both. More data is required to understand electrochemistry and charge transport, because overall redox process depends not only on monomer concentration but also on the nature of the counter ion.

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